GRAFT POLYMERIZATION VIII. EFFECT OF CHANGES IN THE INITIATING SYSTEM ON THE MOLECULAR WEIGHT OF THE GRAFT COPOLYMER IN POLYRETANNED LEATHER

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Abstract

Research was conducted to determine the effects of changes in the initiation system on the grafting of methyl methacrylate onto chromium-tanned sheepskins. The molar ratio of reductant ($NaHSO_3$) to oxidant ($K_2S_2O_8$) was varied over the range of 0.05:1 to 2:1 to study the effect on the molecular weight of the isolated grafted synthetic polymer. This produced a striking effect in terms of bound polymer and its molecular weight. A definite correlation, relating to the grafting efficiency of the leather, was found between the amount of reductant used and the percent polymer bound and extractable homopolymer.

The grafted leathers were exhaustively extracted with ethyl acetate to remove homopolymer, then acid hydrolyzed to remove essentially all of the collagen substrate. Viscosity studies on the isolated grafted synthetic polymers indicated that there is an inverse relationship between the average molecular weight of the graft and the amount of reductant used for grafting at a fixed level of oxidant. The molar ratio giving the highest grafting efficiency was 0.2:1.0, reductant to oxidant.

Introduction

Previous work has demonstrated that: a) collagen can be grafted with vinyl monomers (1–4) and b) the grafted chains can be isolated and their molecular weights determined (5, 6). This paper reports the relationship found between the viscosity molecular weights of the isolated graft chains and the composition of the redox system used during the grafting procedure.

Experimental

Materials. Commercially chromium-III tanned Nigerian sheepskins were graft polymerized with methyl methacrylate obtained from Rohm and Haas

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Company†. The methyl methacrylate contained 10 ppm of the monomethyl ether of hydroquinone (MEHQ) as an inhibitor and was used as received. The 2-butanone was obtained from Aldrich Chemical Co. as a 99+ percent grade. Other chemicals were obtained from a number of sources and used as received.

Graft Polymerization. Pieces of chrome-tanned Nigerian sheepskin weighing approximately 75 g, with an average dry substance of 25 percent, were placed in one-quart Mason jars. To each jar was added an aqueous solution consisting of 800 percent water, 2 percent of the emulsifier Triton X-100, 4 percent potassium persulfate and the appropriate amounts of sodium bisulfite‡, as shown in Table I.

TABLE I

EFFECTS OF MOLAR RATIO OF REDOX SYSTEM ON GRAFT COPOLYMERS

Sample No.	$NaHSO_3$: $K_2S_2O_8$ Molar Ratio	% Polymer Bound (Grafted)	% Polymer Extractable (Homopolymer)	% Total Polymer	Grafting Efficiency	M.W. of Graft	Ave. Moles Collagen per Graft Site
1	0.05:1	17.9	6.5	24.4	73.3	1,678,000	24
2	0.10:1	19.9	6.0	25.9	76.9	1,090,000	14
3	0.25:1	19.6	8.5	28.1	69.7	590,000	7
4	0.33:1	13.1	14.4	27.6	47.5	485,000	9
5	0.5:1	6.4	16.2	22.6*	25.6	350,000	14
6	1:1	2.5	17.1	19.5*	10.0	342,000	37
7	2:1	2.9	15.6	18.6*	11.6	250,000	23

*Values are low due to formation of homopolymer in the float.

All percentages for the float are based on the dry weight of the skins. An oxygen-free atmosphere for the graft polymerization was most conveniently obtained by the use of dry ice. Sufficient dry ice was used to displace all the air, and after the dry ice sublimed, the jars were tightly sealed and tumbled end-over-end for 30 min. All stages of the reaction were carried out at ambient temperatures. At the end of the 30-min period, methyl methacrylate** equal to 33.3 percent by weight of the dry substance was added along with additional dry ice to ensure maintenance of an oxygen-free atmosphere. After the dry ice sublimed, the jars were again sealed, and tumbling was continued for 24 hr, although other studies showed the monomer had disappeared from the aqueous phase of these reactions in only a few hours. Gas chromatographic analysis of the aqueous phase indicated that in each case all but trace amounts of the monomer had been consumed. The

†Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

‡To avoid the release of SO_2, do not contact sodium bisulfite with acids.

**Appropriate care must be taken in handling all monomers because these chemicals may be flammable and toxic.

samples were washed thoroughly in cold running tap water, allowed to dry at room temperature, and ground twice in a Wiley mill with a number 10 screen.

The percent nitrogen was determined by the official semimicro Kjeldahl method. These values were calculated on a moisture- and ash-free basis. The moisture was determined after drying the samples to constant weight in a vacuum oven at 50°C, and the ash values were obtained after ashing the samples at 625°C for two hours.

Homopolymer Extraction. Approximately 7 grams of the air-dried ground samples were weighed into thimbles and extracted in a Soxhlet apparatus for 24 hr with ethyl acetate. A change of solvent was made, and the samples were extracted for an additional 48 hr. Both extracts were evaporated on the steam bath, and the residues were then heated overnight at 100°C, cooled, and weighed. The second extracts contained only trace amounts for each sample, indicating that all of the homopolymer was extracted. The percent extractable was calculated from the combined weight of the extracts.

Acid Hydrolysis. About 3 g of ethyl acetate extracted samples were hydrolyzed by refluxing for 2½ hr in 100 ml of 6 *N* hydrochloric acid. The samples were filtered through sintered glass, washed successively with 0. 2 *N* sodium hydroxide, water, 0.2 *N* hydrochloric acid, and finally water, until the filtrate was neutral. The residues were allowed to air dry for several days.

Viscosity Determinations. The weighed, air-dried residues, after acid hydrolysis, were dissolved in 2-butanone with intermittent stirring for approximately 90 hr at ambient temperature. They were then filtered through sintered glass, washed with several small portions of 2-butanone, and the filtrate and washings were made up to volume so that the final concentration would be between 0.75 and 1.0 g/100 ml. Several dilutions were made for each sample, and the specific viscosities were determined at 30°C by use of a Cannon-Manning semimicro viscometer. The data for the specific viscosities at various concentrations were extrapolated to zero concentration to obtain the intrinsic viscosity necessary for the molecular weight calculation (7).

Results and Discussion

Studies in our laboratory (1–4) on the graft polymerization of vinyl monomers onto hides have been concerned with the optimum conditions for grafting, the physical and chemical properties imparted to the leather by the grafting, and more recently (5, 6) the molecular weights of some of the isolated graft chains. In the present work we determined what effect variations of the molar ratio of reductant to oxidant have on the molecular weights of the grafted synthetic polymers as well as on the grafting efficiency of the reaction. The stoichiometric ratio of the bisulfite/persulfate redox pair is 0.5:1. In all of these experiments the level of persulfate was fixed and the amount of bisulfite was varied above and below

the stoichiometric amount. As the amount of bisulfite was lowered below this ratio, it became the limiting reagent, and smaller and smaller numbers of the primary free radicals, the sulfate anion radical ($SO^{\cdot}_4$), were formed. At levels of bisulfite above the stoichiometric amount, the persulfate was the limiting reagent, which was present at a fixed concentration.

Lowering the amount of bisulfite below the stoichiometric amount had a profound effect on both the molecular weight of the grafted synthetic polymer and the grafting efficiency (Table I). An inverse relationship was found in both cases. Such a relationship is entirely reasonable, since a lower initiator concentration should result in fewer polymerization initiation sites in both the float and on the protein molecule and thus higher molecular weights. And, since the cationic protein has a natural affinity for the sulfate anion radical, it competes successfully with the monomer for the limited amounts of initiator present, and the grafting reaction is favored. The molecular weights of the grafted synthetic polymers obtained with amounts of bisulfite equal to or greater than the stoichiometric amount showed little variation, and the grafting efficiencies were low.

Gas chromatographic analyses showed only traces of methyl methacrylate at the end of the runs. The weight ratio of protein to monomer offered was the same for each sample (1:0.333), so we can calculate the theoretical percent of total polymer in the grafted samples when all of the monomer is converted to polymer:

$$\frac{\%\text{ monomer offered}}{100 + \%\text{ monomer offered}} = \frac{33.3}{133.3} = 25\%$$

Thus, a value of 25 percent for total polymer represents complete conversion of the monomer to homopolymer and grafted polymer.

The percent polymer bound was calculated from Kjeldahl nitrogen determinations on the skin before and after grafting treatment with methyl methacrylate:

$$100 - \frac{\%\text{ nitrogen after grafting}}{\%\text{ nitrogen before grafting}} \times 100 - \%\text{ extractable} = \%\text{ polymer bound}$$

The highest percent of grafted polymer was found in sample #2, indicating that a molar ratio for reductant to oxidant in the region of 0.10:1 is the most efficient for grafting the monomer onto the collagen. The grafting efficiency was calculated from the percent polymer grafted with respect to total polymer, and again sample #2 gave the best results. In a previous study (4), the maximum polymer bound and grafting efficiency were seen at the 0.18 molar ratio. Even though that ratio was not used in the present study, the plots for percent grafted, extractable, and total polymer, and grafting efficiency, as shown in Figures 1 and 2, respectively, bear out those results.

The percent extractable polymer remained relatively constant over the molar ratios 2:1, 1:1, and 0.5:1 (Figure 1). As the molar ratio was decreased further, the percent extractable polymer rapidly diminished. This indicates that there are

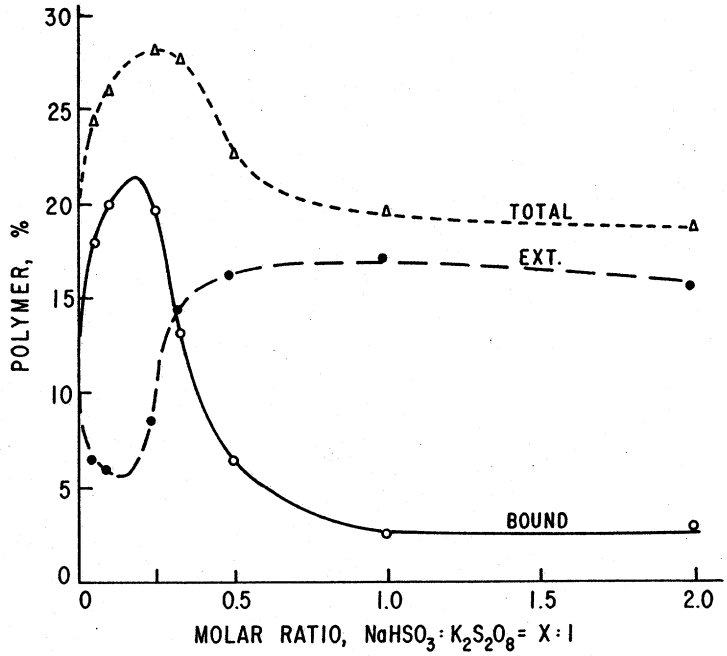

FIGURE 1.—Effect of molar ratio on percent polymer formed (total, bound, and extractable) in the graft copolymers.

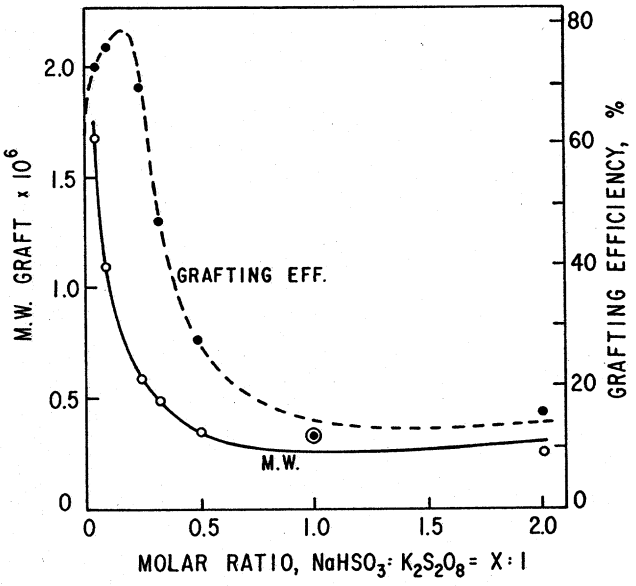

FIGURE 2.—Effect of molar ratio on molecular weight and grafting efficiency of the graft copolymers.

less homopolymers which are by definition not bound to the protein. The two smallest molar ratios used gave the lowest amounts of extractable polymer. It is of interest to note that the computer plot showed a minimum at about the molar ratio 0.18, since the previous report showed a ratio of 0.18 to be the best.

The molecular weight of the isolated graft copolymer and the grafting efficiency are plotted in Figure 2. For samples #3 and 4, the percent total polymer was higher than the theoretical (25%). This can be explained by the following considerations. Since leather is a nonuniform product, we can expect the moisture and protein contents to vary somewhat in different areas of the skin. Comparing the analytical data of the grafted pieces with a control area of the skin under these conditions will undoubtedly lead to some deviation from the expected value.

We can also calculate the average mole of collagen per graft site for each sample:

$$\frac{\text{gm. collagen}}{\text{300,000 M. W.}} \times \frac{\text{graft M. W.}}{\text{gm. polymer bound}} = \frac{\text{ave. moles of collagen}}{\text{graft site}}$$

These values are shown in Table I.

Although amino acid analyses were not determined on the samples used for these molecular weight studies by viscometry, previous results (6, 8) with poly(methyl methacrylate) (PMMA) grafted leathers show that a small peptide was still attached to the amino acid which had provided the grafting site. As determined by amino acid analyses, this peptide amounted to <0.2 percent (W/W) of the isolated graft of PMMA. That amount of peptide should have only a minimal effect on the viscosity of the polymer. Based on these considerations, the method should be valid at least on a comparative if not absolute basis.

In summary, these studies show certain effects of the initiating system on the graft copolymers formed and give some further direction for the ideal system to produce PolyRetan Leather. We can conclude that the best initiating system for this level of persulfate has a molar ratio of between 0.10 and 0.25:1 for sodium bisulfite to potassium persulfate. This is shown by the plots for percent polymer bound, grafting efficiency, and percent extractable in Figures 1 and 2. As the amount of bisulfite drops below the stoichiometric ratio, there are fewer free radicals formed on the collagen and in the float. This gives rise to increasingly higher molecular weights for the graft copolymers and higher grafting efficiencies. Consideration of these factors should benefit tanners economically when producing leather by the PolyRetan process.

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